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LOW TEMPERATURE X-RAY DIFFRACTION
INVESTIGATION OF EMBRITTLED MINIMUM SIGNATURE
CHAPARRAL PROPELLANT

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The Army has been developing a minimum signature propellant motor for an improved CHAPARRAL air defense weapon system since 1975. As part of validation and qualification, the motor was subjected to a diurnal temperature cycling test during FY78 to simulate field temperature storage conditions. The special cycling test consisted of 30 cycles of 24 hours each from 283°K (50°F) to 347°K (165°F) followed by 30 cycles of 24 hours each from 283°K to 219°K (-65°F). Inspection of smokeless CHAPARRAL motors after 30 cold cycles revealed severe propellant grain cracking that, because of the increased burning surface, could result in catastrophic motor failure upon firing. This type of grain failure, with randomly located cracks, had not previously been found in other minimum signature propellants under development or in conventional double-base propellants used in Army tactical missiles.

Because of the uniqueness and seriousness of the problem, and its potential impact on production of the CHAPARRAL minimum signature propellant motor, an intensive program was initiated jointly by the Army Propulsion Directorate [1] and the propulsion contractor, Hercules Incorporated [2], to determine the cause of the grain failure and solve the problem. A number of possible failure mechanisms were proposed and investigated. The CHAPARRAL propellant involved in the grain failure is comprised of glycerol trinitrate (nitroglycerine) plasticizer; a crosslinked binder of polyglycoladipate, nitrocellulose and polycaprolactone; a solid oxidizer; and inorganic additives. A primary failure hypothesis was that the nitroglycerine plasticizer or the crosslinked propellant binder was crystallizing during cold temperature cycling, resulting in propellant embrittlement and subsequent grain cracking. The grain, in either event, would inevitably crack because it would not have sufficient strain capability to withstand thermal cycling.

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Low temperature x-ray diffraction research on crystallization phenomena in nitrate ester plasticized smokeless propellants and gumstocks was conducted by the Army Propulsion Directorate in support of the CHAPARRAL Project Office. The Propulsion Directorate had previous x-ray diffraction analysis experience with binder crystallization phenomena in other types of propellants that facilitated the CHAPARRAL propellant research. The objective was to determine the possible roles of both nitrate ester, particularly nitroglycerine, and binder low temperature crystallization in CHAPARRAL propellant embrittlement. A number of variables such as moisture content, propellant surface contamination, conditioning temperature, and energetic plasticizer mixtures were investigated for their influence on nitroglycerine crystallization in propellants and gumstocks. The details of the investigation are described in this paper.

The results of the low temperature x-ray diffraction research showed unequivocally that low temperature CHAPARRAL propellant embrittlement is caused by nitroglycerine crystallization. Having established the cause of embrittlement, an alternative propellant, containing a mixed plasticizer of nitroglycerine and 1,2,4-butanetriol trinitrate was developed by Hercules, Incorporated in cooperation with the Army Propulsion Directorate. This alternative minimum signature formulation has undergone extensive low temperature thermal cycling without embrittling, and is expected to replace the original minimum signature propellant formulation in future CHAPARRAL XM121 smokeless motor production.

EXPERIMENTAL

Instrumentation

An x-ray diffractometer marketed by Philips Electronic Instruments was used. Copper $K\alpha$ radiation was produced by a high intensity copper target x-ray tube operated at 35 kV constant potential and 30 mA. The copper $K\beta$ component of the x-ray tube output was reduced with a lithium fluoride monochromator. The copper $K\alpha$ radiation was collimated with a 1° divergence slit. Voltage to the x-ray generator was stabilized with a 5 kVA line voltage stabilizer. The recorder was a Sargent-Welch Model SR. The diffracted copper $K\alpha$ x-ray intensity was measured with a scintillation detector. The associated electronic circuit panel (type 12206/0) has a linear/log rate meter, a decade scaler with an electronic timer, and a pulse height analyzer.

To permit periodic low temperature x-ray diffraction analyses of samples over an extended period of time, a temperature controlled attachment, constructed earlier for binder crystallization studies,

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was modified slightly for this application. The design, which is described in detail elsewhere [4], is based on that of Sakurai and Suzuki [5]. Commercially available attachments are not suitable for this application, because they are not designed for the effective transfer of samples at low temperatures. The attachment was insulated with Styrofoam. The copper K α radiation passed through a 180° opening in the attachment chamber that was sealed with two layers of Mylar film separated by an air space. Frost was prevented from collecting on the outer Mylar window by blowing air over its surface. The attachment was connected by means of an insulated tube to a 12-liter Dewar flask containing liquid nitrogen. The temperature within the attachment was capable of being cooled to well below the required 219°K in a short period of time by passing cold nitrogen gas around the sample. The nitrogen gas was generated by applying voltage to a resistor suspended in the liquid nitrogen, by means of a variable transformer. The temperature in the attachment was controlled by manual adjustment of the transformer and read with a digital thermometer. The most important feature of the attachment is that it can be easily disassembled and reassembled at low temperatures for the insertion and removal of samples.

Procedure

All propellant and cured gumstock samples were cut into slices measuring 2.54 cm x 3.81 cm with thicknesses varying from 1.5 - 3 mm. The cured gumstock was composed of all of the propellant ingredients except the solids. Various samples were preconditioned at equilibrium relative humidities of <1%, 20%, 44%, 58%, and 81% for the evaluation of moisture effects on low temperature brittleness. The equilibrium relative humidity of <1% was achieved by drying with 4A molecular sieve, and the others were achieved by equilibration of the samples in sealed vessels containing appropriate salt solutions. Each sample was placed against an aluminum plate having the same dimensions and the sample and plate were tightly wrapped with aluminum foil. The other wrapped sample surface was then placed against a second aluminum plate. A clamp was placed on each end of the sample so that it was tightly sandwiched between the plates, thus preventing contamination from the sample storage environment. Some samples were thermally cycled from 283°K to 219°K whereas others were stored at constant temperatures of 255°K (0°F), 233°K (-40°F), and 219°K.

Samples were periodically removed from the conditioning boxes and transferred to the x-ray diffractometer on dry ice. The low temperature attachment was precooled to 219°K and then rapidly disassembled and reassembled for sample insertion and analysis. During sample insertion in the attachment, the sample surface collected

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a thin film of frost, and the internal temperature of the attachment warmed to approximately 273°K. Upon reassembly, the sample temperature was rapidly cooled to the 219°K test temperature so that no possible nitroglycerine or binder crystallites melted. The thin film of frost on the sample surface rapidly sublimed in the dry nitrogen environment. The mounted sample at 219°K was continuously scanned at 2° per minute, generally over the range of 10-40° 2θ with a rate meter time constant of 1 or 2 seconds and a full scale recorder sensitivity of 1000-2000 counts/second.

RESULTS AND DISCUSSION

Temperature and Moisture Effects

Propellant and gumstock samples were temperature cycled daily from 283°K to 219°K to duplicate the condition under which minimum signature propellant in CHAPARRAL motors embrittled. The samples were also equilibrated to different moisture levels because previous surveillance data indicated a possible dependence of propellant embrittlement on moisture content. The primary purpose of constant temperature storage at 219°K, 233°K, and 255°K was to insure that any binder crystallization that might occur would be detected. Thermal cycling to 283°K would likely melt binder crystallites, based on previous experience [3]. Also, different constant storage temperatures would provide valuable information on nitroglycerine crystallization initiation and propagation rates. The crystallization of nitroglycerine is a two step process involving initiation (nucleation) and propagation (crystal growth). If either step is prevented, the propellant will not embrittle. Initiation can occur homogeneously within the nitroglycerine itself or heterogeneously by external nucleating materials. Both types of nucleation were considered.

The baseline x-ray diffraction pattern of amorphous CHAPARRAL propellant gumstock at 219°K is shown in Figure 1. Only weak diffraction peaks from ice on the sample surface are evident for crystalline material. In contrast to the amorphous gumstock diffraction pattern, the pattern for crystallized nitroglycerine in gumstock is shown in Figure 2. The two largest peaks were recorded off-scale to bring out the weaker peaks in the pattern. The interplanar d-spacing in angstroms of each peak is noted by the peak. The intensities of the second and third largest peaks relative to the most intense peak (I/I_1) are also noted on the pattern. This particular sample had been cycled between 283°K and 219°K for 36 days. Typically, the average induction time for the initiation of nitroglycerine crystallization during this temperature cycle was found to be about 30 days, but the actual time varied substantially.

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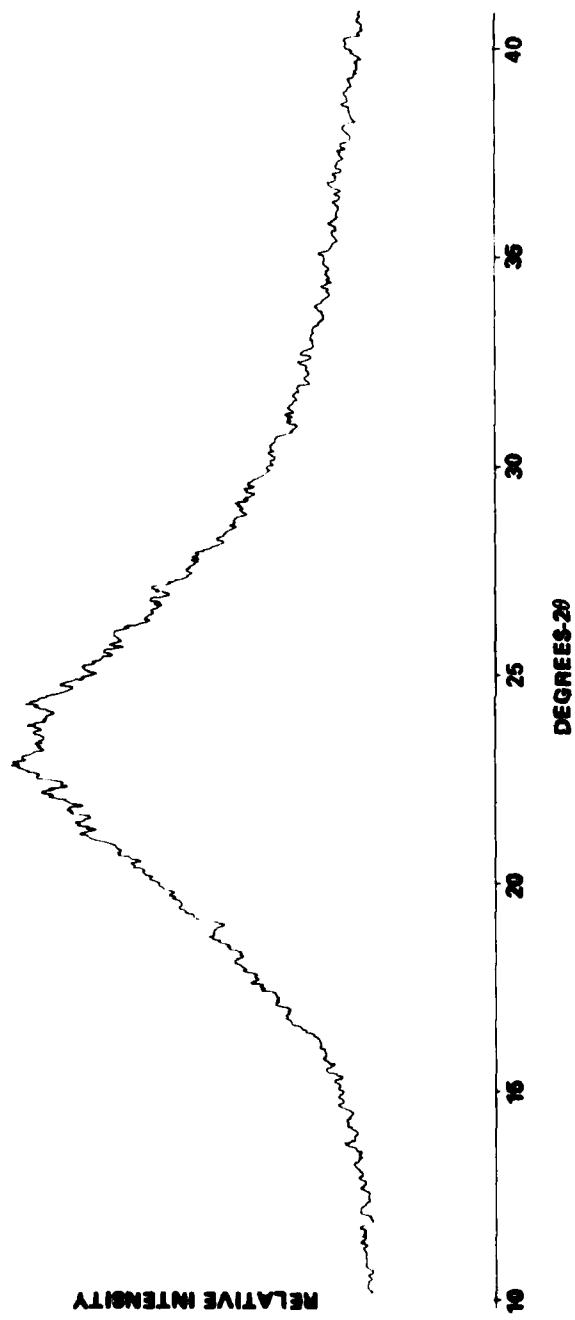


Figure 1. X-ray diffraction pattern of amorphous CHAPARRAL propellant gumstock at 219°K (-65°F).

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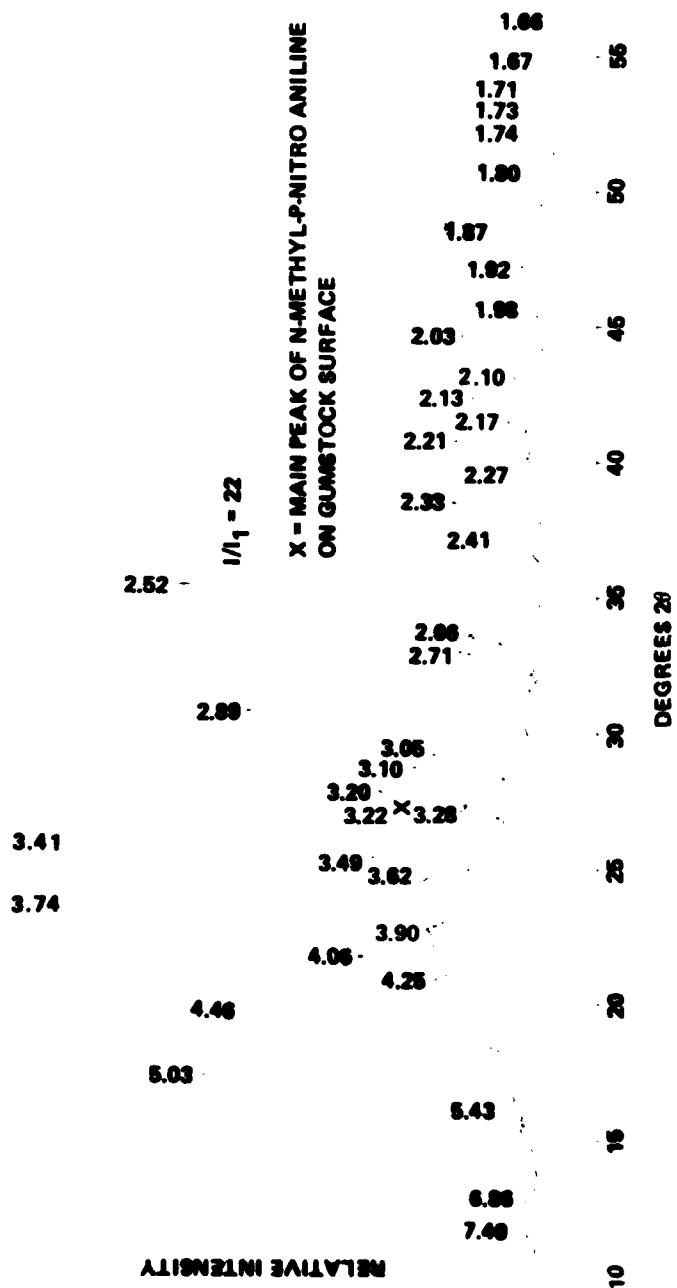


Figure 2. X-ray diffraction pattern of crystallized nitroglycerine (stable form) in embrittled CHAPARRAL propellant gumstock.

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When the diffraction pattern shown in Figure 2 was first observed, it was clear that a large amount of crystalline material had formed and that it was most likely nitroglycerine. An immediate identification from the pattern could not be made, however, because x-ray diffraction data on crystallized nitroglycerine is not available in the literature. Consequently, a neat sample of the nitroglycerine was crystallized at 244°K (-20°F), by seeding with a portion of the embrittled gumstock, and analyzed. Except for unavoidable preferred orientation of crystallites in the neat nitroglycerine, the pattern agreed with that in Figure 2 and thus confirmed that the nitroglycerine in the gumstock had crystallized. That the embrittled gumstock seeded the neat nitroglycerine crystallization is evidence itself that the nitroglycerine had crystallized in the gumstock during thermal cycling.

Neat nitroglycerine when cooled is viscous and readily supercools, and therefore is very difficult to crystallize without seeding. This might account at least partially for the long induction period for nitroglycerine nucleation. Once nucleation occurs, however, crystal growth is rapid during thermal cycling. The optimum temperature regions for both nucleation (219°K-233°K) and crystal growth rates (244°K-250°K) were included in each temperature cycle.

The x-ray diffraction pattern in Figure 2 is that for the stable form of nitroglycerine that melts at about 286°K. The x-ray diffraction pattern of embrittled CHAPARRAL propellant that was also cycled between 219°K and 283°K for 36 days is shown in Figure 3. The peaks of crystallized nitroglycerine are superimposed on those of the propellant crystalline solids, but are clearly discernible. This data showed conclusively that CHAPARRAL propellant embrittlement is due primarily to nitroglycerine crystallization at low temperature.

The effect of propellant and gumstock moisture content on the time required for nitroglycerine to crystallize during temperature cycling from 219°K to 283°K is given in Table 1. The time for crystallization or the induction period definitely increases as the moisture content decreases. In fact, samples that were predried over molecular sieve 4A (< 1%) did not embrittle when stored for the maximum test time of 8.1 months. This suggests that the propellant embrittlement problem might be solved by insuring that propellant in CHAPARRAL motors is initially dry and maintained dry during storage. This is not considered a practical solution because of the low moisture levels required, and the fact that heterogeneous nucleation could still possibly occur from extraneous material such as dust. The sample in this investigation was protected from the environment. If nucleation occurs, then crystal growth will proceed rapidly. A better solution would be to assume that nucleation will occur and to significantly reduce subsequent growth by kinetic means. This is the approach

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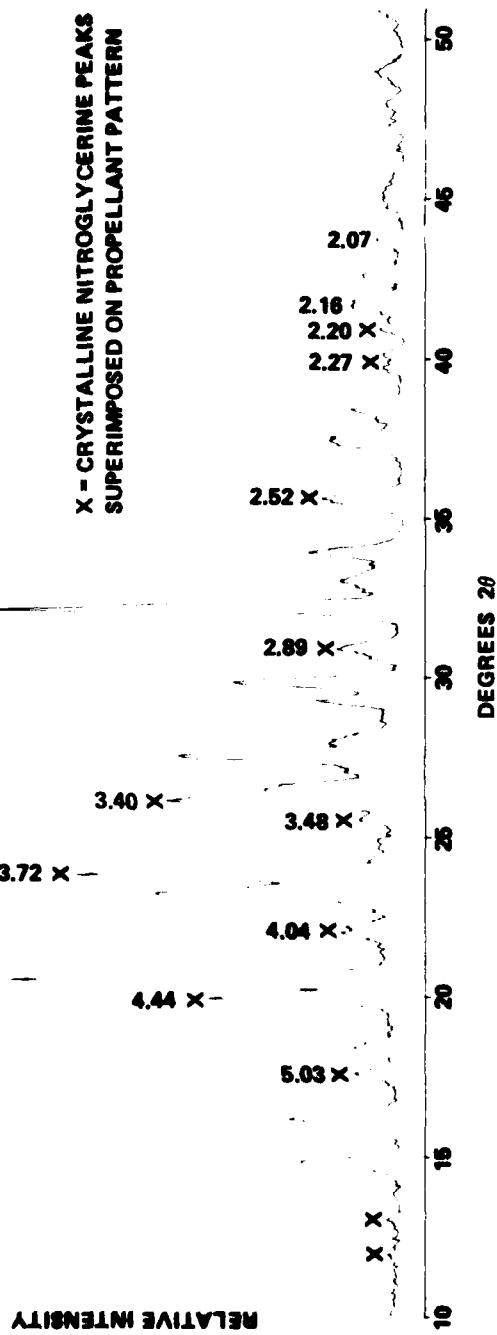


Figure 3. X-ray diffraction pattern of embrittled CHAPARRAL propellant showing crystalline nitroglycerine peaks.

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TABLE 1. EFFECT OF MOISTURE ON CHAPARRAL PROPELLANT AND
GUMSTOCK NITROGLYCERINE CRYSTALLIZATION (TEMPERATURE
CYCLED DAILY FROM 283°K TO 219°K)

Sample Equilibrium Relative Humidity, %	Moisture Content, Wt %		Months for Nitroglycerine Crystallization	
	Gumstock	Propellant	Gumstock	Propellant
* <1	<0.005	<0.002	~8.1	~8.1
20	0.120	0.049	4.2	3.3
44	0.265	0.108	3.1	2.7
58	0.350	0.143	3.3	2.3
81	0.488	0.199	1.5	1.5

* Samples dried over 4A molecular sieve desiccant.

usually used [2] to solve the crystallization problem. Nevertheless, as a result of these and other data, stricter moisture controls were instituted during propellant and motor manufacture and motor storage.

The role of moisture in CHAPARRAL propellant embrittlement was not clearly established, but it appears that ice crystals forming within the propellant might act as sites for heterogeneous nitroglycerine nucleation. The induction period for the formation of internal ice crystals, which was readily detected by the x-ray diffraction analysis, generally preceded nitroglycerine crystallization by a short period of time.

The effect of constant temperature storage on the time for nitroglycerine crystallization to occur in propellants and gumstocks is shown in Table 2. At 219°K no crystallization occurred up to the maximum test period of 4.2 months. As expected, the times for crystallization at 233°K and 255°K were longer than for samples of the same moisture content that were temperature cycled. The stable form of nitroglycerine was formed at 255°K (see Figure 2) whereas what is believed to be the labile form was initially observed at 233°K. The labile form slowly converted to the stable form after 1 to 2 months

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storage. The x-ray diffraction pattern of a propellant lacquer sample seeded with a portion of gumstock sample embrittled at 233°K (see Figure 4) illustrates the labile nitroglycerine form. Only the 4.17A peak is easily discernible in embrittled propellant. Lacquer is similar to gumstock, but is not crosslinked.

TABLE 2. EFFECT OF CONSTANT TEMPERATURE STORAGE ON NITROGLYCERINE CRYSTALLIZATION IN CHAPARRAL PROPELLANT AND GUMSTOCK

<u>Storage Temperature, °K</u>	<u>Equilibrium Relative Humidity, %</u>	<u>Months for Nitroglycerine Crystallization</u>	
		<u>Propellant</u>	<u>Gumstock</u>
255 (0°F)	81	---	3.6
233 (-40°F)	81	2.4	2.9
233 (-40°F)	44	>3.2	---
219 (-65°F)	81	>4.2	>4.2

Special Investigations

A number of special investigations were conducted to further elucidate the mechanism of nitroglycerine crystallization and subsequent propellant embrittlement. A summary of propellant and gumstock samples with various plasticizer and polymer combinations is given in Table 3. Polyglycoladipate polymeric binder, which is used in CHAPARRAL propellant, was not found to crystallize during either temperature cycling or constant temperature storage. A candidate polyethyleneglycol binder, however, did crystallize to a large extent in gumstock, but no evidence of crystallization could be found in propellants.

During previous thermal cycling, N-methyl-p-nitroaniline (MNA), a propellant ingredient, was observed to form on gumstock surfaces. The rate of formation and the amount formed was proportional to the sample moisture content. The MNA did not form on samples stored at constant temperature. It was suspected that MNA might initiate nitroglycerine crystallization on the sample surface. Three types of samples were analyzed for the influence of MNA: a) normal gumstock samples, b) gumstock samples with MNA omitted from the formulation, and c) gumstock samples with additional MNA added to the

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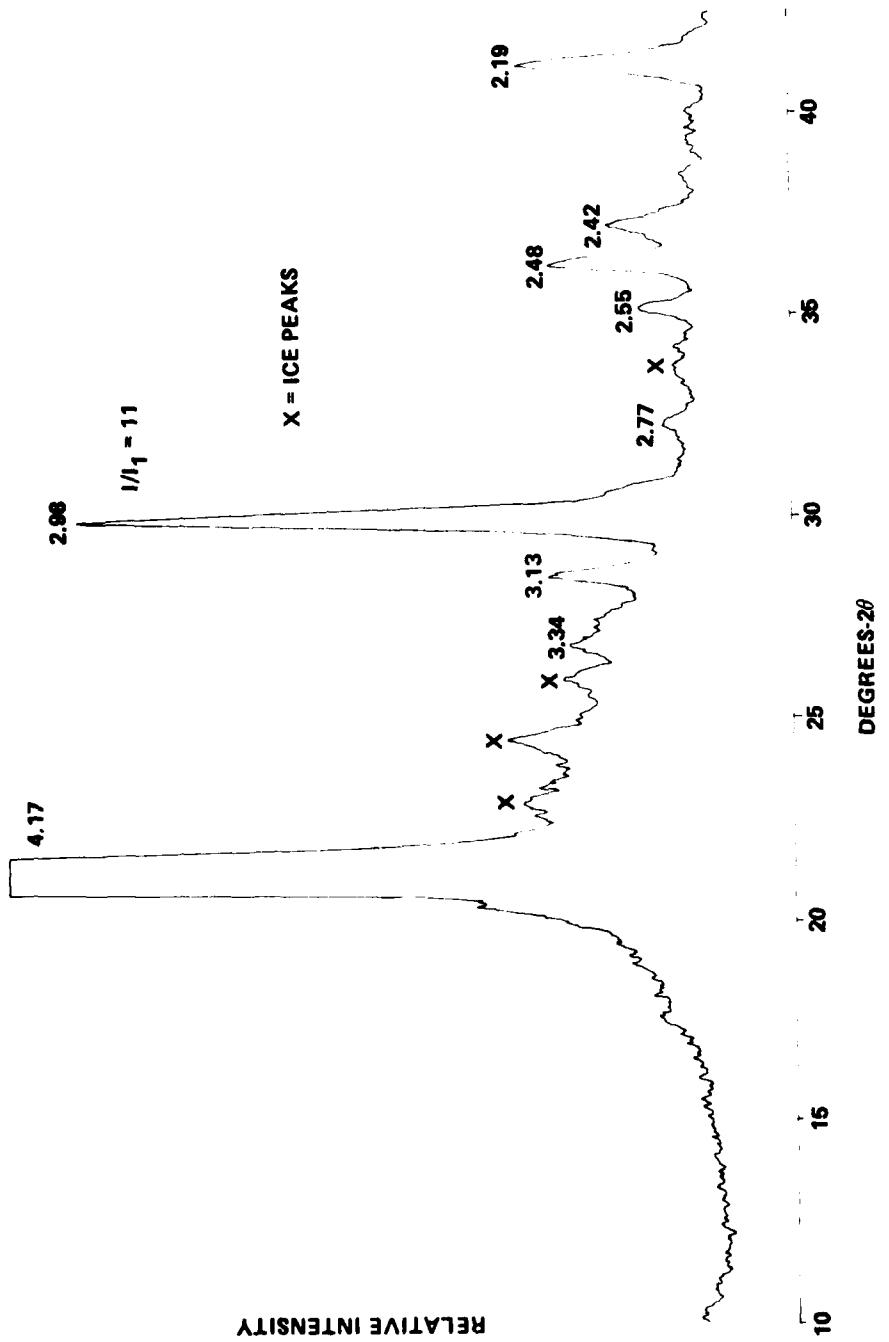


Figure 4. X-ray diffraction pattern of crystallized nitroglycerine (labile form) in CHAPARRAL propellant lacquer.

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TABLE 3. PLASTICIZER/POLYMER COMBINATIONS INVESTIGATED IN CHAPARRAL CANDIDATE PROPELLANT AND GUMSTOCK FORMULATIONS

Polymer	a. Plasticizer	Type Sample	Low Temperature Crystallization	
			Plasticizer	Polymer
Polyglycol- adipate	NG	Propellant	Yes	No
	NG	Gumstock	Yes	No
	None	Gumstock	Yes	No
	NG	Gumstock (No PCP)	Yes	No
	NG	Gumstock (No MNA)	Yes	No
	NG	Gumstock (MNA added to Surface)	Yes	No
	NG + BTTN	Gumstock	No	No
Polyethylene- Glycol	TMETN	Propellant	Yes	No
	TMETN + DEGDN	Propellant	No	No
	TMETN + DEGDN	Gumstock	No	Yes
	TMETN + BTTN	Propellant	No	No
	BTTN + TMETN + DEGDN	Propellant	No	No

a. Plasticizer mixtures were equal weight proportions

NG = Nitroglycerine

PCP = Polycaprolactone

MNA = N-methyl-p-nitroaniline

BTTN = 1,2,4-Butanetriol Trinitrate

TMETN = Trimethylolethane Trinitrate

DEGDN = Diethylene Glycol Dinitrate

surface. These samples were investigated as a function of moisture content during temperature cycling from 219°K to 283°K. The results showed that MNA in the presence of moisture significantly reduced the induction time for nitroglycerine crystallization over that for moisture alone, but it was not a primary causative factor for propellant embrittlement.

Nitroglycerine crystallization can be initiated both homogeneously and heterogeneously by extraneous materials, and the subsequent crystal growth rate is rapid. Consequently, the only

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practical solution to the embrittlement problem was to change the plasticizer composition to one that either could not be crystallized thermodynamically, or to one that upon initiation would have a negligible crystal growth rate. The latter approach, using a plasticizer mixture of nitroglycerine and 1,2,4-butanetriol trinitrate in a 1:1 weight ratio, was chosen. The thermodynamic solution was not possible, because the freezing points of acceptable pure plasticizers and plasticizer mixtures are above the lower temperature limit for the CHAPARRAL motor. The six plasticizer mixtures shown in Table 3 were evaluated for their crystallization properties during 219°K to 283°K cycling and constant storage at 233°K. No plasticizer crystallization was found in these mixtures after extensive temperature conditioning even when the samples contained a high percentage of moisture.

CONCLUSIONS

The x-ray diffraction research demonstrated unequivocally that low temperature embrittlement of the original minimum signature CHAPARRAL propellant was caused by crystallization of the nitroglycerine plasticizer. The exact mechanism of nitroglycerine crystallization was not established, but several parameters that influence the rate of initiation or nucleation of nitroglycerine were identified. Propellant moisture in particular increases the rate of initiation in proportion to the moisture content. A propellant component, N-methyl-p-nitroaniline, which forms on the propellant surface, further decreases the time to initiation in the presence of moisture. The propellant binder, which was initially suspect, shows no evidence of crystallization at low temperature.

Low temperature x-ray diffraction analyses of plasticizer mixtures that did not crystallize upon extended low temperature storage demonstrated the feasibility of this approach for solving the embrittlement problem. A modified minimum signature CHAPARRAL propellant, containing a mixed plasticizer of nitroglycerine and 1,2,4-butanetriol trinitrate, is undergoing requalification and has successfully withstood extensive low temperature cycling without embrittlement.

The x-ray diffraction research is significant because it established the cause of the embrittlement problem and evaluated selected approaches for solution of the problem, thus enabling a confident, rapid solution without seriously impacting CHAPARRAL XM121 motor production. Furthermore, fundamental data on low temperature propellant crystallization phenomena were obtained that will enhance future minimum signature propellant development programs.

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